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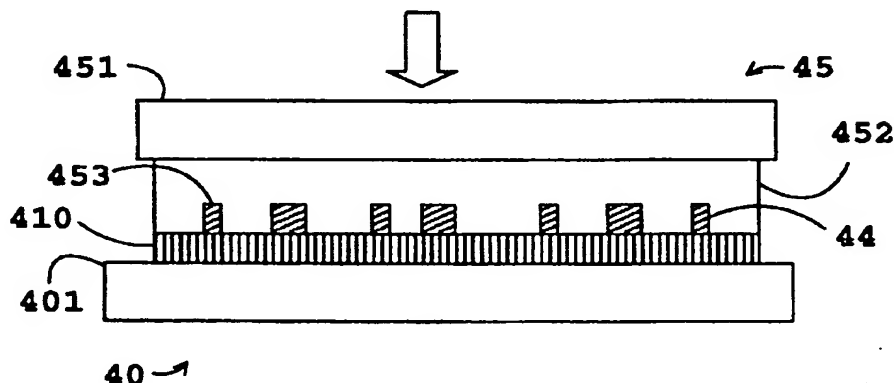
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(54) Title: LITHOGRAPHIC SURFACE OR THIN LAYER MODIFICATION



(57) Abstract

A process for producing lithographic features in a substrate layer is described, comprising the steps of lowering a stamp (15) carrying a reactant (14) onto a substrate (10), confining the subsequent reaction to the desired pattern, lifting said stamp and removing the debris of the reaction from the substrate. Preferably, the stamp carries the pattern to be etched or depressions corresponding to such a pattern. Using the described methods, patterns with submicron features can be generated. The method allows a general solution to parallel handling and transfer of materials in a variety of technical fields.

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DESCRIPTION**Lithographic Surface or Thin Layer Modification**

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The present invention is directed generally toward a lithographic process, involving the modification of the surface of a substrate at precisely determined areas, thus creating a lithographic pattern on the substrate. It relates particularly to producing structured layers for use in the manufacturing of electric and electronic devices, such as integrated circuits, displays, storage media, sensors, and the like. More specifically, the invention relates to an etching step within such a lithographic process.

15

BACKGROUND OF THE INVENTION

Though the current invention is also applicable to lithographic processes as used in printing industry, the current invention is mainly concerned with lithography as applied in the production of electronic and electric devices, sensors, and the like. The characteristic length scale, i.e. the design rule of the relevant lithographic pattern is usually in the micron to submicron region. The manufacturing process of these devices is currently almost entirely dominated by methods based on optical or e-beam lithography.

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Since the emergence of integrated circuits (ICs) and micromechanical devices, optical lithography has been crucial for the purpose of their mass production: Its convenience, parallel operation and resolution has created a huge market. Fabrication of devices with ever smaller dimensions, necessary to satisfy the demands of storage and computation, becomes increasingly problematic with visible light as processes steadily reach fundamental limits, predominantly set by diffraction. This realization triggered intense research in UV, X-ray, e-beam, and Scanning Probe (SP)

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1 lithography. These methods deliver high resolution with varying success
and their economics remain, at best, uncertain. Reasons for these
uncertainties include limitations due to wavelength dependent phenomena,
the slow writing speeds of e-beam and SP lithographies, and challenges in
5 finding appropriate resists and masks.

A separate and related limitation of current lithographies is the complexity
of processes required for modifying or altering a layer at regions defined by
the desired lithographic pattern to be written; lithography today relies on
10 bulk transfer of reactive material from the liquid or gas phase, or from a
plasma using masks to protect the other regions of the substrate.

An alternative approach to lithography has been published by A. Kumar
and G.M. Whitesides in : Appl. Phys. Lett. 1993, 63, 2002- 2004. In this
15 process, known as microcontact stamp lithography, stamps are fabricated by
casting a replica in poly(dimethylsiloxane) (PDMS) of a master with a
negative of the desired pattern. In the one known example of microcontact
stamping used for lithography, the PDMS stamp is inked with an alkanethiol,
hexadecanethiol, and transferred to gold by transient contact between the
20 stamp and the gold substrate. The thiol covalently binds to the gold in an
autophobic reaction: the thiol modifies the wettability of the gold substrate,
preventing spread of the bulk liquid phase and thus confining the
transferred monolayer to the region of contact between raised the regions of
the elastomeric stamp and the substrate. The presence of these thiols
25 allows subsequent lithographic processing of the gold using a cyanide/
oxygen etch that selectively removes gold not protected by a monolayer of
alkanethiol. Although this system allows reproductions of features in gold
down to one micron, its scope remains limited to a special subset of useful
materials, i.e. thiols and gold.

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In all these lithographic processes, a number of agents are used which pose
a considerable potential threat to the environment. Huge efforts are
therefore taken to sufficiently protect workers within IC factories and the

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1 population living in their surrounding from a possible exposure to these agents. Immense resources are also invested for safely depositing the waste and remains of the IC manufacturing.

5 The object of the present invention is to avoid limitations in the type of reactions, materials transferred and range of substrates useful in contact based lithography and to demonstrate new strategies of direct processing of substrates without the intervening application of resists.

10 It is a further object of the invention improve the known lithographic processes by providing a method for modifying a surface at precisely determined positions. While being more convenient to apply, the new process should at least have a resolution comparable to state-of-the-art lithography. Another object of the invention is to restrict the amount of
15 agents and material used in the lithographic process, it particular should hazardous waste generated by this process be minimized.

As mentioned above, lithographic processes are also found in the field of printing. In particular, color printing is found to face similar problems
20 concerning alignment during several separated printing steps as encountered in lithography for semiconductor devices. In four color printing the colors cyan, magenta, yellow and black are applied to four separate printing rollers that transfer the lithographic pattern to the paper four separate printing steps. The alignment among those four printing steps
25 limits the maximal resolution and quality of color images especially on cheap and low quality paper. Printing can either be done with poor alignment (~ 0.1 mm) and bad image quality on cheap paper or with better alignment (~ 0.01 mm) and better image quality on high quality paper. The rastering dimension has to be adapted to the alignment and consequently is
30 > 0.1 mm (< 300 dpi) for low quality paper and > 0.01 mm (< 3000 dpi) for the paper with the highest quality. Photographic reproduction, on the other hand, can be carried out with grain sizes of the order of microns ($<$

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1 0.001 mm). Thus, high quality printing requires expensive equipment able to maintain tolerances of 10 microns over several meters.

It is therefore seen as another object of the invention to improve the
5 conventional color printing procedure, in particular to facilitate the alignment procedure necessary to print several colors.

SUMMARY OF THE INVENTION

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The object of the invention is achieved by a method and a stamp as set forth in the appended claims.

Herein the term substrate is used as a synonym for the layer of material to
15 be altered or transformed by the lithographic process. The term reaction is meant to include chemical reactions, etching or dissolving reactions, as well as modification by physical processes such as diffusion. A deformable or an elastic layer is preferably defined as a layer having a Young's modulus in the range 10^4 , more preferably $0.25 \cdot 10^6$ to $5 \cdot 10^6$ dyne/cm². Suitable
20 materials having this property could be poly(butylidene), poly(dimethylsiloxane), poly-(acrylamide), poly(butylstyrene) and co- or block-polymers, thereof. A conformal contact between two surfaces accommodates the unevenness of both surfaces. In addition to the elastic layer, the stamp may comprise a support structure and/or layers of rigid
25 material. A stamp according to the present invention should not be restricted to a basically flat form. It may take on other shapes, such as rollers or half-spheres.

A process according to the present invention transforms the substrate
30 material by either a chemical reaction, such as etching, or by the diffusion of a dopant. The substrate or layer to be modified is thus not exposed to an atmosphere, plasma or immersed into a bulk solution containing the reacting substance or dopant. The present invention is characterized in that

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1 the reactive substance or dopant is transferred to the surface of the
substrate by contact printing with the soaked or wetted stamp.

The reaction can be confined to a desired lithographic pattern by several
5 methods:

In a first variant of the invention, the stamp has, within the desired range of
accuracy, a flat surface and, thus, makes contact with the substrate along its
entire supporting surface. The stamp confines the reactant strictly to the
10 interface between stamp and substrate. No reactant is released into the
surrounding. A pattern-wise reaction is achieved by either patterning the
substrate in a previous lithographic step such that only the pattern area is
affected by the subsequently applied reactant, or by using a mask which
covers a part of the substrate from the stamp, exposing only the other,
15 unprotected part to the reactant.

Within the interface layer itself, at regions of the substrate not protected
from the reactant by the previous lithographic step or the mask, a reaction
commences. At other regions of the substrate, which are either inert or
20 protected, transfer of the reactant from the stamp to the substrate stops
after a very short period. In case that the mask is etched away by the
reaction, care has to be taken to choose its thickness such that the reactant
does not contact the substrate at the protected areas within the exposure
time. The unprotected areas of the substrate are immediately exposed to the
25 reactant through the holes in the mask.

The new reaction process is controlled by a proper selection of the stamp
material, of the participant in the reaction to be applied to the stamp, and of
the resist material or mask. The process is further controlled by the amount
30 of reactant provided to the reaction zone by the stamp, the pressure exerted
on the stamp, the contact time, and the temperature at the interface between
stamp and substrate. By adjustment of these parameters, it is for example
possible to adapt the penetration depth of an etching reaction to the

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1 thickness of the layer to be etched. In particular, use can be made of
self-passivation occurring when the first molecular layers of the substrate
react with the reactant as provided by the stamp, forming a protective layer
for the substrate material beneath. As the thickness of this passivation layer
5 is dominated by diffusion, the reaction process can be very conveniently
controlled by the temperature. Also, autophobic reactions may be used to
confine the reaction zone. The new process is favorably applied when the
layers to be modified are thin, e.g. below 100 nm.

10 In another preferred embodiment of the invention, the reaction is confined
to the lithographic pattern by patterning the surface of the stamp such that it
reproduces the desired pattern on the surface of the substrate. The features
of the pattern on the stamp are formed as protrusions, soaked or wetted
with the reactant. It is an advantage of this embodiment of the invention
15 that no mask or protective coating is required to produce a desired pattern
on the substrate. The reactant is confined to those regions of the substrate
which are to be modified; thus reducing the applied amount of the reactive
agent. A pattern can be written to the stamp by any known lithographic
process, including e-beam lithography, UV-VIS lithography, and lithography
20 employing a scanning probe microscope (SPM lithography), by the method
described in Kumar et al., or by using the stamp lithographic process as
described herein. Another advantage of this embodiment of the invention is
that materials, in particular organic materials such as being used for thin
film displays, can be modified directly without having to apply a photoresist
25 coating.

The reactive agent preferably is an etchant used to etch the desired features
into the substrate. In yet another preferred embodiment, the patterned
surface of the stamp carries a catalyst, thus confining the reaction zone to
30 the immediate vicinity of areas in which the catalyst is present.

A further preferred embodiment of the invention utilizes a new approach to
pattern transfer using conformal contact between surfaces: While in the

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1 previous embodiments, the surface of the stamp carries the reactant, in
present embodiment of the invention ideally the surface is free from the
reacting substance, and instead microcontainers, such as wells, trenches,
depressions, or recesses, are filled with the reactant. These
5 microcontainers can be formed as replicas of lithographically formed
masters that contain a negative image of the desired microcontainers, in a
pattern of arbitrary complexity and with individual volumes set by the sizes
of protrusions in the masters. These microcontainers, preferentially formed
from an elastomer, hold an etchant, reactant, or a material for subsequent
10 parallel chemical processing. The substance in these containers is
preferably held in place using differential wetting between the interior and
exterior of the containers, e.g., a substance is confined to the inside the
container by rendering its interior hydrophilic and the surrounding surface
areas hydrophobic.

15

When an array of elastomeric microcontainers is brought into contact with a
surface, the areas of the elastomer between the reliefs that form the
microcontainers come into molecular contact with the substrate as
described by Chaudhury and Whitesides (Science 1992, Vol. 255, 1230-1232).
20 This molecular, or conformal, contact, provides a tight seal between the
microcontainer and the substrate so that the contents of the microcontainer
attack the substrate only through the openings of the microcontainers.
Confinement of the processing step occurs as a consequence of the
molecular seal between the elastomer and substrate and not by autophobic
25 reaction as described in Kumar et al., so a wide range of reactants and
processing strategies are possible on a variety of substrates that includes,
but is not limited to, gold, aluminum, silicon, strontium titanate, plastics, or
glass. Direct processing using microcontainers does not require a resist
layer so that this form of lithography is simpler than contact lithography
30 based on the known stamping or other conventional lithographies based on
light or electron beams. Since the microcontainers rely on contact, the
wavelength of light is not a limitation in achieving ultimate resolution with
this technique.

1 Because the volume of each microcontainer in the array is independent of
the others, i.e., the amount of material transferred locally to the substrate is
constrained to the size of the microcontainer allowing processing to occur to
different extents in adjacent regions. Thus microcontainers allow
5 convenient three dimensional processing of substrates in applications where
heterogeneous topologies are required. Since the contents of
microcontainers are independent of each other, a subset of microcontainers
in an array can hold one type of agent whereas other subsets of the
containers hold a different agent. This type of differential filling of the
10 microcontainers is readily achieved using patterned elastomeric lids with
openings keyed to the underlying microcontainers. The pattern in these lids
allows selective access to the microcontainers so that they are filled
differentially using a series of patterned lids. Thus the contents of
microcontainers with different agents, or combinations of agents, are
15 simultaneously transferred to the substrate in a single processing step.

Hence, in this embodiment of the invention recesses or depressions in the
surface of the stamp are used as microcontainers for storing the participant
in the reaction, while the the surface does not carry any agent. It is seen as
20 a major advantage of this embodiment of the invention that the reaction
zone is inherently sealed by those protruding parts of the surface of the
stamp when the stamp is pressed onto the surface of the substrate. The
method has the potential of delivering an improved resolution compared to
the known methods and the above-mentioned embodiments. The use of this
25 embodiment of the invention is not limited to surface modification but can
well be applied for depositing material onto the substrate. By use of a
selective filling procedure, such as adapting the shape and/or by modifying
the properties of the the faces of the microcontainers, or by using a mask or
lid to cover selected containers, as described above, different materials can
30 be brought in contact with the substrate simultaneously. Besides
accelerating a lithographic process, this embodiment can also be applied for
simultaneously preparing, screening or testing of a large number of
samples, such as drugs or new compounds for superconducting devices. In

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1 addition, it was found that the selective filling of microcontainers in an elastomeric stamp can also advantageously be used in conventional color printing.

5 It is further contemplated to use the herein described method for transferring an dopant to the surface of the substrate. By heating the interface between the stamp and the substrate, the dopant diffuses into the bulk material of the substrates. As this method requires a heat-resistive matrix or stamp material. Heating of the stamp however can be avoided
10 by transferring a very high concentration of the doping agent, which diffuses at low temperatures into the substrate material. Then the stamp is removed and the substrate is heated such that the dopants diffuse deeper into the bulk material of the substrate.

15 These and other novel features believed characteristic of the invention are set forth in the appended claims. The invention itself however, as well a preferred mode of use, and further objects and advantageous thereof, will best be understood by reference to the following detailed description of illustrative embodiments when read in conjunction with the accompanying
20 drawings.

DESCRIPTION OF THE DRAWINGS

25 The invention is described in detail below with reference to the following drawings:

FIG. 1 illustrates schematically an etching process in accordance with a first embodiment of the invention.

30

FIG. 2 illustrates schematically an etching process in accordance with a second embodiment of the invention.

- 1 **FIG. 3** illustrates schematically a catalytic reaction in accordance with
a third embodiment of the invention.
- 5 **FIG. 4** illustrates schematically an etching process in accordance with
a fourth embodiment of the invention using microcontainers.
- 10 **FIG. 5** illustrates schematically an etching process in accordance with
a variant of the fourth embodiment of the invention.
- 15 **FIG. 6** illustrates schematically an etching process in accordance with
a variant of the fourth embodiment using microcontainers with
different depths.
- 20 **FIG. 7** illustrates schematically a process in accordance with a variant
of the fourth embodiment using microcontainers for a selective
deposition on a substrate.
- 25 **FIG. 8** illustrates schematically another process in accordance with a
variant of the fourth embodiment using microcontainers for a
selective deposition on a substrate.
- 30 **FIGs. 9, 10** illustrate schematically the use of a process in accordance with
a variant of the fourth embodiment using microcontainers for a
selective deposition on paper for color printing.

MODE(S) FOR CARRYING OUT THE INVENTION

Referring to Figs. 1A and 1B, a first example in accordance with the
invention is shown, in which a protective layer of hexadecanethiol **110** is
transferred to a base layer **101** of gold using a patterned stamp inked with
the hexadecanethiol solution in ethanol. Details of this procedure are
described in the above cited prior art. Subsequently, another stamp **15** with

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1 an essentially flat contact area is wetted with mixture of cyanide (CN) and
potassium hydroxide (KOH) 14. This agent is brought in contact with the
protective coating 110 by lowering the stamp 15 onto the substrate 10. The
stamp comprises a solid base plate 151 and a layer of the elastic polymer
5 poly(dimethylsiloxane) (PDMS) 152, which accommodates the unevenness of
the substrate. The PDMS layer 152 is wetted with the etchant 14 after being
made hydrophilic by its brief contact with an acid or reactive plasma. In
contact with the coating 110, the etching process starts at the unprotected
regions 111 while the rest of the coating remains, at least to a large extent,
10 inert against the etchant 14. When the etching process is terminated, the
stamp 15 is lifted and the substrate is rinsed with water to remove the
debris. The substrate after the rinsing is shown in Fig. 1B. The gold layer
101 is removed with a speed of approximately 10 nm/min at the unprotected
areas. A considerably smaller amount of etchant is released into the
15 environment by this process than by all known etching processes.

Another example of an etching process in accordance with the invention is
illustrated by Fig. 2A. In this example, no patterned coating or mask is
required as the pattern is transferred along with the etchant 24 by a stamp
20 25 with a patterned surface layer 252 onto the substrate 20. The patterned
layer 252 is fabricated as a replica of a patterned photoresist layer. A
PDMS elastomer is cured on top of this photoresist layer, and then adhered
to a suitable substrate 251 and peeled off the photoresist. Using this
method, submicron lithographic pattern can be reproduced. The pattern of
25 the stamp 35 is wetted carefully with mixture of nitric acid (HNO₃) and
hydrochloric acid (HCl) 24. A lesser amount of etchant than in the previous
example is required to wet or soak the protruding pattern features. For
etching the stamp is brought into close contact with a gold covered silicon
substrate 30. After etching a pattern of gold 210 is left on the surface of the
30 silicon 201, as is shown in Fig. 2B.

A patterned stamp is also used in the example illustrated by Figs. 3A and
3B. In this example of the invention, the pattern is covered by a layer of

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1 platinum 34. The silicon substrate 301 is covered by an azido-terminated
self-assembled monolayer (16-azidohexadecanethiol, $\text{HS} - (\text{CH}_2)_{16} - \text{N}_3$) 310.
The platinum covered stamp 35 is brought into contact with the silicon
substrate 30 in a solution of isopropanol saturated by hydrogen. Transient
5 contact between the protrusions covered by platinum catalyst 34 and the
substrate causes a conversion of the azido functional group to an amine
only where the platinum makes direct contact with the surface 311. Because
this catalytic reaction occurs on all parts of the patterned surface
simultaneously, one second is sufficient to ensure effective conversion on
10 an arbitrarily large area 311. For comparison, the method of Muller et al.,
published in Science 268 (1995), 272-273, to produce lithographic pattern of
amino-terminated thiols, which is inherently sequential and relies on STM
control to position the metal catalyst, requires 126 minutes to convert a 100
mm² area.

15
An alternative method to control the application of direct chemical reaction
is to fill the reactants 44 into microcontainers 453, as is depicted in Figs. 4A
and 4B. These microcontainers are well, trenches, recesses or depressions
of the surface 452 of the stamp 45. The reactant solution does not
20 contaminate the surface of the stamp but is deposited into the wells or
trenches patterned into the surface of the stamp. The microcontainers 453
preferably have at least one dimension, i.e. length, width, or depth, in the
submicron region. Embedded in the elastic matrix 452 of the stamp, it is
possible to bring all microcontainers simultaneously into contact with the
25 surface of the substrate. A particularly convenient way to fill these
microcontainers is by self-assembly of the liquid into these containers based
on the differential wettability of the surface: a microcontainer for example
may comprises a hydrophilic base and/or sidewalls while the surrounding
surface of the stamp is hydrophobic. A liquid will thus be held by capillary
30 forces in the hydrophilic regions and be easily removed from the
hydrophobic regions by, for example, shear forces.

1 These containers can preferentially be realized using a composite stamp
structure as shown in Fig. 5A. The composite stamp comprises two layers
of material, wherein the first layer 551, forming the base of the
microcontainer 553, is hydrophilic and the second layer 552, forming the
5 sidewalls of the microcontainer 554 and the surface of the stamp, is
hydrophobic. An aqueous solution 54 wets the surface as shown in Fig. 5A.

In a further embodiment of this variant of the invention, the wetting
properties of the preformed microcontainers are directly controlled by
10 exposing them through a mask 51 to a vapor or plasma 541 of a reactive
species that changes the chemical characteristic of the exposed region (Fig.
5B). The mask provides openings 511 for the direct passage of this vapor or
plasma, or alternatively allows selective passage of light that activates the
surface or a reactive gas, which in turn is used to modify the surface. The
15 mask 51 is made preferentially from an elastomer with the appropriate
openings that makes conformal contact with the underlying stamp, thus
establishing a leakproof seal.

The property of an elastic layer to form a leakproof seal when pressed onto
20 another surface is also exploited when the stamp 55 with the
microcontainers is brought into contact with a substrate 50. The surface of
the stamp acts as mask and protects the surface where conformal contact is
made, sealing it from the contents 54 of the microcontainers. Moderate
vertical forces on the stamp bring the surface of the liquid film into
25 patterned contact with the substrate and trigger the start of the process (Fig.
5C). If the filling of the microcontainers consists for example of an etching
agent, the substrate is left with depressions in the exposed regions (Fig.
5D).

30 In a similar manner, electrochemical processes could be carried out when
layer 551 is either an ionic or metallic conductor. A convenient way of
preparing patterned electrodes is to form a thin patterned layer of elastomer
on top of a metal, conductive polymer or ionic gel. The thin layer of

1 elastomer again provides conformal contact and thus a leakproof seal
between the bottom electrode and the substrate, simultaneously electrically
insulating these regions.

5 The penetration depth of the etchant, or in general the impact of any surface
reaction induced by this method, can further be controlled by the filling
volume of the microcontainers. This type of control leads to a stamp design
where the trenches 652 are formed with varying filling level or with varying
depth, as illustrated by Fig. 6A. The new process provides a method for the
10 formation of truly three dimensional topography or profiles in a substrate 60
using a single lithographic processing step (Fig. 6B).

Another example of this formation of 3D structure is a chemical or an
electrochemical reaction that deposits a solid material on top of the
15 substrate. The volume of reactant in the microcontainer and the shape of the
microcontainer can both be used to determine the shape of the resulting
features.

In addition to building or removing structures on the substrate, the new
20 contact process can be used to modify the material properties like
wettability, or dopant concentration or chemical identity in the exposed
regions of a substrate, as the type of reaction depends only on the
participants in the reaction, i.e., for a given substrate on the filling of the
recesses or microcontainers. In addition to processes involving liquids,
25 these novel containers for chemical reactions are also applicable to
processes involving gas, gels, and solids on a wide variety of substrate
types. The volume of the containers provide strict and flexible control over
the extent and type of reactions. The shape of the containers controls the
patterned transfer.

30

It is further contemplated to use microcontainers for a discriminant
self-assembly of preformed solid parts 74 for subsequent transfer to the
substrate 70, as schematically illustrated by Figs. 7A-7D. Shape recognition

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1 of these solids could further be refined by a selective modification of the walls 752 and bottom 753 of the microcontainers. For example, a hydrophilic/hydrophobic face 741 on the solid would enhance preorientation of this solid with a similar matching hydrophilic/hydrophobic face 753 in a
5 microcontainer. Further refinement would result from the use of specific ligand-receptor complexes. Complementary strands of DNA provide a particularly robust example of this type of ligand-receptor interaction used as a "glue" to attach a preformed solid in an oriented manner in a microcontainer. The solids 74, themselves, could be molded within the
10 microcontainer by deposition or reaction processes prior to their transfer to the substrate 70 (Figs. 7C,D).

The description to this point has focused on homogeneous reactions carried out within the volume of unique microcontainers. It is however further
15 possible to carry out simultaneously different reactions by selective filling of these microcontainers. This selective filling can be achieved by placing patterned "lids" 81 on top of the array of microcontainers, as shown by Fig. 8A-8C. The openings 811 in these patterned lids allow selective passage of gas, liquids or solids into a subset of the microcontainers. By controlling the
20 size of the openings, the flux of material into different microcontainers is controlled in a single processing step. Changing the patterned lid 81 allows access to an alternative subset of microcontainers (Figs 8B, 8C), resulting in a differential filling of the total array.

25 In the example of Fig. 8, each three adjacent microcontainers of an array are filled with different substances. These could for example be phosphors with different light emission. The contents of the containers can be further processed or transferred directly to the substrate. An additional masking step could provide a differential set of electrical contacts by transfer of a
30 plating solution or evaporation from a effusive source. As the lids and the pattern can be produced with a resolution of below 1 micron, this methods can be used, for example, for manufacturing of high-definition flat panels.

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1 The selective filling of microcontainers in an elastomeric stamp can also be
applied to conventional color printing. Instead of four separate print masters
which carry the colors cyan, magenta, and yellow, together with black, only
one print master with microcontainers is required when using a selective
5 filling process as described above.

The schematic setup for a printing process is illustrated by figures 9 and 10.
The printing master roller 95, which carries an elastic layer 951 with
microcontainers, is surrounded by four color rollers 941-944 having half of
10 the diameter of the master roller and four cleaning rollers 945. Each color
roller transfers one of the colors cyan, magenta, yellow and black to the
printing roller 95 through a lid layer 91. The lid layer has openings only to
those microcontainers of the printing roller, which are to be filled with the
respective color. The cleaning rollers 945 wipe the surface of the printing
15 roller. After the loading of the microcontainers, their contents is transferred
to the paper 96.

The color printing is hence performed in one step largely eliminating the
need for alignment, except for the one between the master and the four lid
20 rollers. For this alignment, the use of self- or inherent alignment means are
possible, such as mutually corresponding protrusions and recesses on both
types of rollers.

The filling and printing procedure is further illustrated by Figs. 10 A-F. The
25 figures show the plane which includes the center axis of the printing roller
95 and the center axis of each of the four color rollers 941-944, respectively,
along the respective contact line between both rollers. For each color
(including black) 1040, the lid layer 1010 of a color roller opens the passage
to the respective microcontainers 1051 in the printing master layer 1050. The
30 microcontainers of Fig. 10 have a different shape to distinguish the different
colors. Figures 10E and 10F illustrate the color transfer to the band of paper
1060.

1 In a variant of this embodiment, a color mixing is achieved with lids on
different color drums which provide access to the same set of
microcontainers such that the mixing occurs within each of these containers
before their contents is transferred to the paper.

5 The maximal contrast of printed images can be enhanced since the amount
of transferred color can not only be determined by the diameter of the
microcontainers but also by their depths. A typical contrast for a
microcontainer diameter ratio of 1:8 is 512 instead of 64. The sizes of the
10 microcontainers can vary between 0.3 micron, given by the self-alignment
and 3 micron. This results in a resolution of 8500 dpi and a contrast of
1:1000, well in the range of color photography. The requirements concerning
tolerances and accuracy of such equipment are stricter than those for
conventional instrumentation, but are limited to one set of printing roller
15 with four ink rollers.

Since contact lithography as being the main concern of the present
invention allows reduction of most of the process in semiconductor
fabrication to printing-like steps, the stamp may take the shape of a printing
20 roller contacting wafers attached to a transport medium. Especially
applications where the coarse alignment accuracy before self-alignment
does not need to be better than 10 microns, like printing of flat panel
polymer LED displays could be handled by this process analogously to the
printing of paper as described above.

25 Another example demonstrating the usefulness of the concept of
microcontainers as described herein is found in the field of preparing and
screening of liquid and solid materials, e.g. therapeutic agents. Single
agents with known efficacy often have increased effectiveness (lower
30 toxicity) when used in conjunction with other agents of a similar or different
class of compounds. With the selective or differential filling, a wide range of
such combinations can be prepared enabling an effective search for
optimum mixtures. This search is carried out directly in the volume of the

1 microcontainer by homogenously adding a solution of the target to all
microcontainers and carrying out an assay. For the preparation or
screening of a combinatorial array, a series of lids is required, which cover
different regions of the stamp surface. Such a set of lids may cover half, a
5 quarter, an eighth, and so forth, of the microcontainers.

By varying for example the amount and composition of precursors for a
superconducting compound in each microcontainer using said series of lids,
the resulting solids (from sintering or another reaction) would have a
10 stoichiometry that reflects the original starting concentrations of the
precursors. Since important material properties of these bulk solids are
known to be tremendously influenced by composition (superconductivity,
elastic modulus, reflectivity, crystallinity, etc.), this method provides a
practical way to synthesize "libraries" of compounds with systematic
15 variation of single parameters. In further process steps, these samples, each
being the content of one microcontainer, can be transferred as a pattern to a
substrate by pressing this substrate to the surface of the microcontainer
stamp. By contacting each compound with metallic contacts, batch
measurements of the critical temperature and other parameters of a
20 superconductor can be performed.

Compared to known processes in which the different reactions have to be
performed sequentially, the possibility of carrying out several reactions
simultaneously provides an inherent alignment of the simultaneous
25 processes and reduces the necessary equipment. The presence of
microcontainers also allows combinatorial syntheses with good separation
to neighboring microcontainers. The reduced number of processes carried
out on the final surface reduces the amount of processing time and
susceptibility to contamination.

30

In the following, an example combining several of the above described
alternatives and embodiments of the present invention is presented. A
microcontainer plate is formed with an array of regular circular depressions

1 300 nm deep and 10 micrometer in diameter by pouring a prepolymer of
polydimethylsiloxane (PDMS) onto a silicon master with the negative of
these features and curing the polymer. In parallel, a second silicon
substrate is prepared that has a patterned set of openings keyed to the
5 array of circular depressions. These openings transit the entire thickness of
this silicon wafer, which is 10 micrometer, forming a perforated silicon lid.
This silicon lid is a single crystal protected by a thermal oxide of two
nanometer thickness, which is maintained as a hydrophilic surface by
rinsing with acid.

10

The PDMS microcontainer plate, supported on a glass substrate, is aligned
to the openings in the previously described silicon lid using a three axis
mechanical aligner. On alignment the supported PDMS microcontainer plate
is allowed to contact the silicon lid under its own weight so that a releasable
15 adhesive interaction occurs between the elastomeric plate and the lid. This
assembly is turned over and placed within a chamber for exposure to an rf
water plasma (10-2 mbar $\text{H}_2\text{O}/\text{Ar}$) for 15 minutes, thus rendering the
interiors of the microcontainers hydrophilic but not the regions between
these containers which are masked by the silicon lid.

20

The assembly is removed from the chamber and a drop of 10% buffered HF
placed directly on top of the openings in the silicon lid. The containers are
filled by capillary action; brief (10 sec) treatment with ultrasound (sonication)
ensures consistent filling. The lid is removed by fixing the glass support
25 that holds the microcontainer plate in an aligner and gently lifting off the
silicon wafer. A silicon wafer with a 20 nm thick chemical oxide is brought
down into contact with the microcontainer plate with sufficient force (appr.
 0.005 N/cm^2) to cause a 1% deformation in the thickness of the PDMS
microcontainers bringing the liquid in the microcontainers into contact with
30 the silicon substrate. The reaction is allowed to proceed for 30 seconds and
the pressure is released from the silicon wafer, which is withdrawn and
rinsed with water.

1 The etched oxide layer provides a patterned mask suitable to allow differential etching of the underlying silicon following exposure to base as described with reference to Fig. 1. The volume of HF used to open the SiO₂ protective layer is approximately 100 femtolitre per hole or 0.1 microlitre for
5 a million holes. The patterned oxide layer of the substrate is exposed to an unpatterned hydrophilic stamp made from PDMS with a modulus of 10⁵ dyne/cm² soaked in 1: 1 isopropanol / (30% KOH water) for 30 minutes. The reaction is allowed to proceed at 70 C for 1 minute to etch a set of 200 nm deep holes in the silicon in a pattern that matches the pattern of openings
10 in the oxide layer. This "bulk" processing step requires only a few hundred microliters.

As an extension to the above method a microcontainer stamp is formed by curing PDMS with a modulus of 5*10⁶ dyne/cm² on top of a wafer with
15 silicon protrusions of varying height. Thus the microcontainers in the stamp have different volumes that reflect the height of the protrusions in the master as shown in Fig. 6. A patterned perforated lid is formed and contacted to the microcontainer plate, and rendered hydrophilic as described above. The microcontainers are filled with 10% KOH in water. An
20 unpatterned silicon wafer with its thermal oxide removed by exposure for 1 minute to buffered HF is brought into contact with the microcontainer plate and held with a force of 0.005 N/cm². The dissolution of the underlying silicon is allowed to proceed until the volume of KOH in the deepest containers is exhausted.

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CLAIMS

1. Method for modifying a surface of a substrate (10; 20; 30; 40) by a reaction, comprising the steps of
 - 5 - applying at least one participant (14; 24; 34; 44) in said reaction to a stamp (15; 25; 35; 45) comprising a deformable material (152; 252; 352; 452);
 - bringing said stamp into conformal contact with said substrate; and
 - confining the reaction to a predefined lithographic pattern.
- 10 2. The method of claim 1, wherein the reaction is confined to the lithographic pattern by a mask (110).
3. The method of claim 1, wherein the reaction is confined to the
15 lithographic pattern by using a stamp (35) with a surface patterned in accordance with said lithographic pattern.
4. The method of claim 1, wherein the participant in the reaction is an etching agent (24).
- 20 5. The method of claim 1, wherein the participant in the reaction is a catalyst (34).
6. Method in accordance with claim 1, comprising the steps of
 - 25 - filling the at least one participant (44) in the reaction into depressions (453) in a surface of the stamp (45) with the deformable layer (452), said depressions forming the predefined lithographic pattern; and
 - bringing said stamp into conformal contact with the substrate such that the surface of said stamp forms a seal around the openings of said
30 depressions, effectively confining said reaction in accordance with said predefined lithographic pattern.

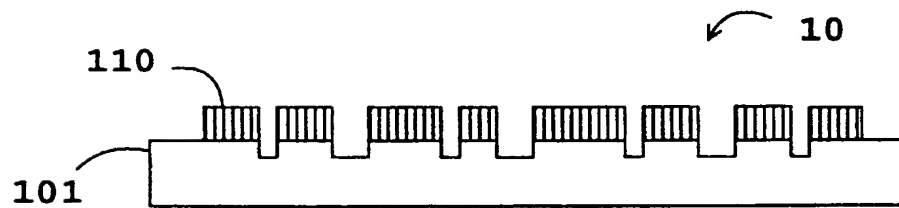
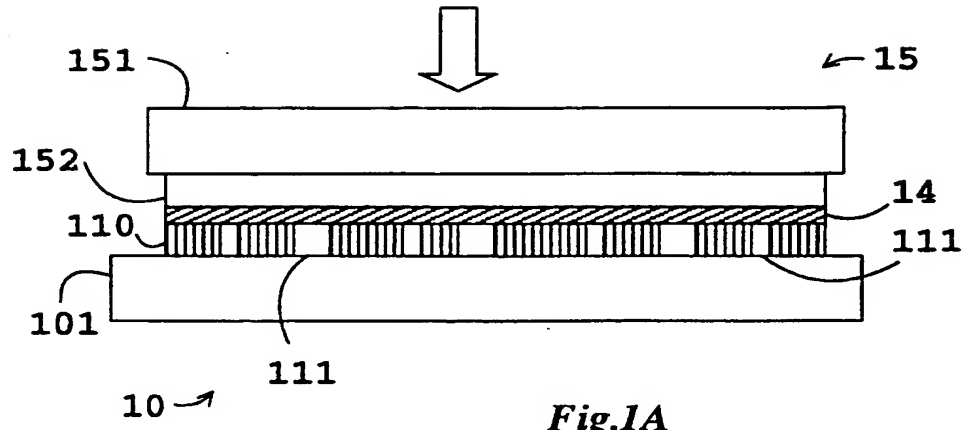
- 1 7. Method in accordance with claim 6, characterized in that a face (553, 554) of the depressions has a higher affinity towards a solution than the surface of the stamp (55).
- 5 8. Method in accordance with claim 6, characterized in that the depressions (652; 752) have varying depths and/or cross sections.
9. Method in accordance with claim 6, characterized in that the depressions are filled with different materials (841-843).
- 10 10. Method in accordance with claim 6, characterized in that the depressions are filled with different materials (841-843) by using at least one mask (81) covering a part of said depressions.
- 15 11. Device, especially an integrated circuit, a light emitting diode (LED), or a liquid crystal diode (LCD), or a flat panel display produced by a method in accordance with any of the previous claims.
- 20 12. Color printing method in accordance with claim 6, comprising the steps of
- filling at least two different colors into depressions in a surface (951) of a printing roller (95) with a deformable layer (951), said depressions forming a predefined print pattern; and
 - bringing said printing roller into conformal contact with a printing medium (96), in particular paper, such that said surface of said printing roller forms a seal around the openings of said depressions, effectively confining the color transfer in accordance with said predefined printing pattern.
- 25 13. The method of claim 12, characterized in that each color (1040) is filled into separate depressions (1051).
- 30

- 23 -

- 1 14. The method of claim 12, characterized in that at least two different colors are mixed in a single depression before being transferred to the printing medium (96).
- 5 15. Etching process for lithography, in particular for submicron lithography, comprising the steps of transferring an etchant (14) to a stamp (15) and bringing said stamp into contact with the layer (110) to be etched, lifting said stamp and removing the debris of the etching reaction from said layer.
- 10 16. The etching process of claim 15, characterized in that the stamp (25, 35) comprises a patterned layer (252, 352).
- 15 17. The etching process of claim 15, characterized in that the stamp (25) comprises a layer (252) with protrusions, said protrusions carrying the etchant (24).
- 20 18. The etching process of claim 15, characterized in that the stamp (45) comprises a layer (452) with depressions (453) being at least partly filled with the etchant (44).
- 25 19. Apparatus for modifying a surface of a substrate (10; 20; 30; 40) by a reaction, said apparatus being characterized by
- a stamp structure (15; 25; 35; 45) carrying at least one participant (14; 24; 34; 44) in said reaction and comprising at least one layer of a deformable material (152; 252; 352; 452) for bringing said stamp structure into conformal contact with said substrate; and
 - means for confining the reaction to a predefined lithographic pattern.

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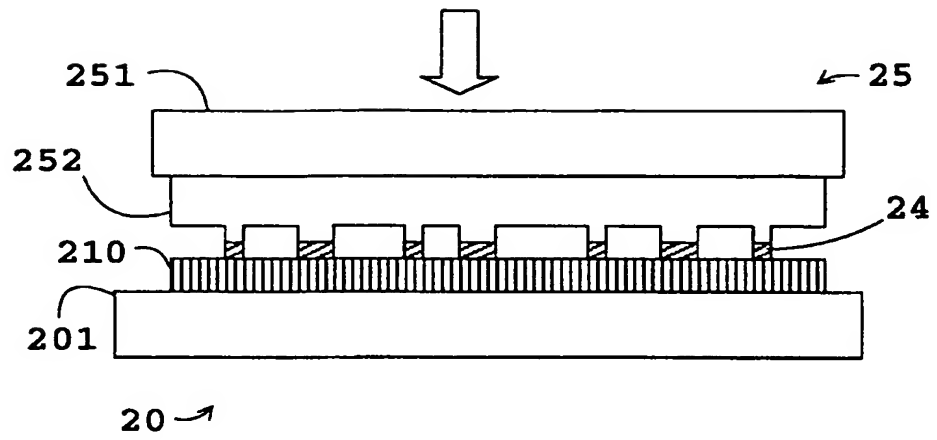


Fig.2A

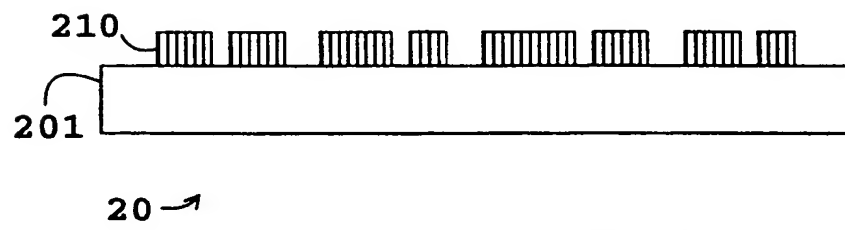


Fig.2B

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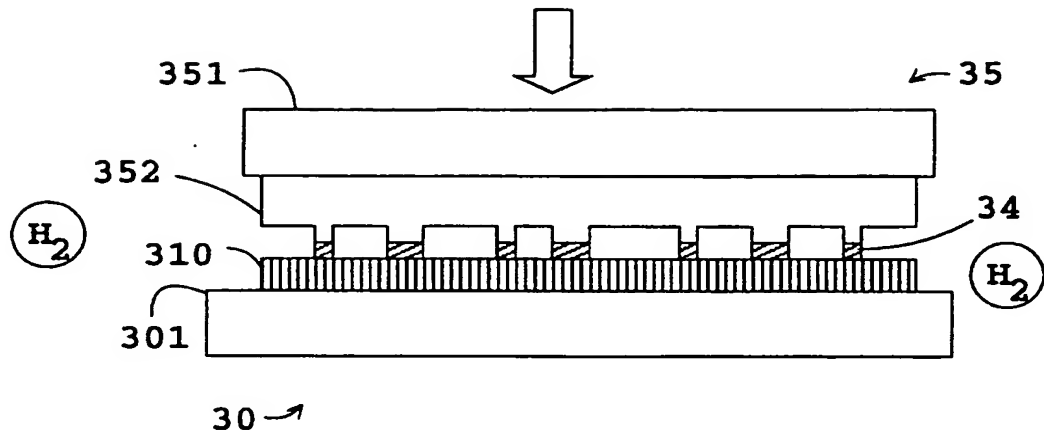


Fig.3A

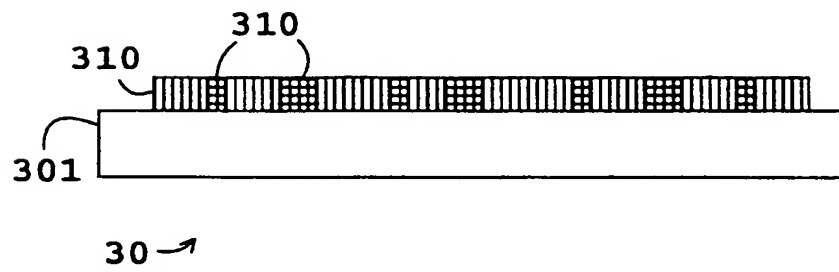


Fig.3B

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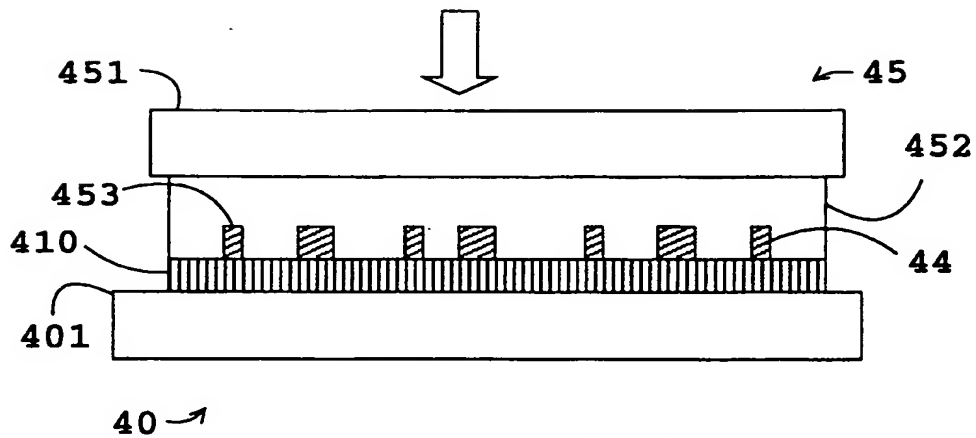


Fig. 4A

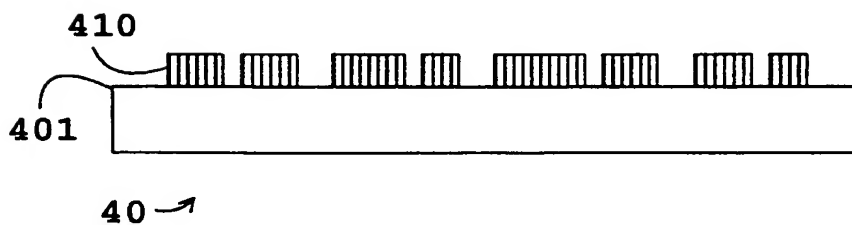
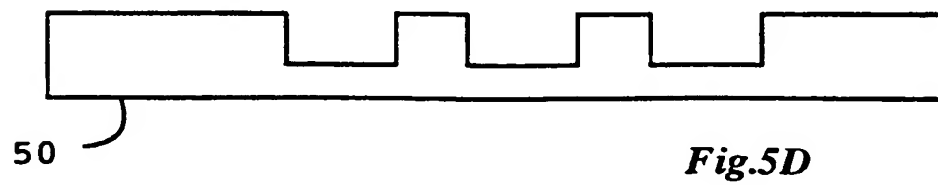
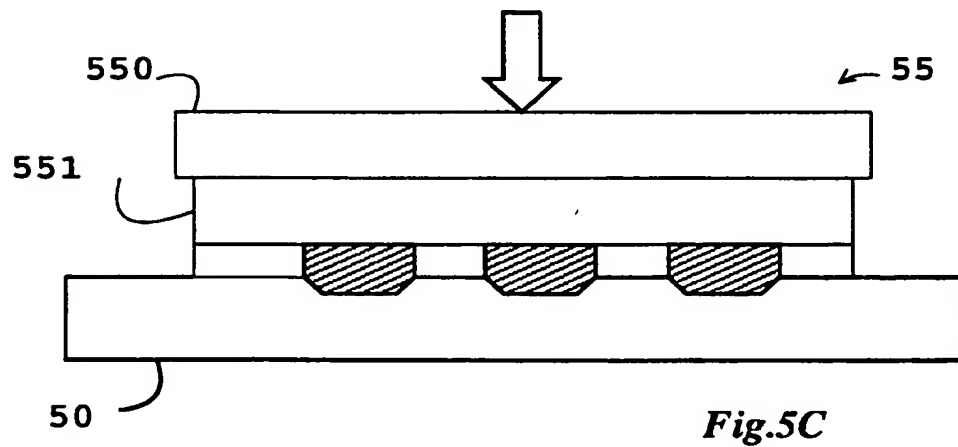
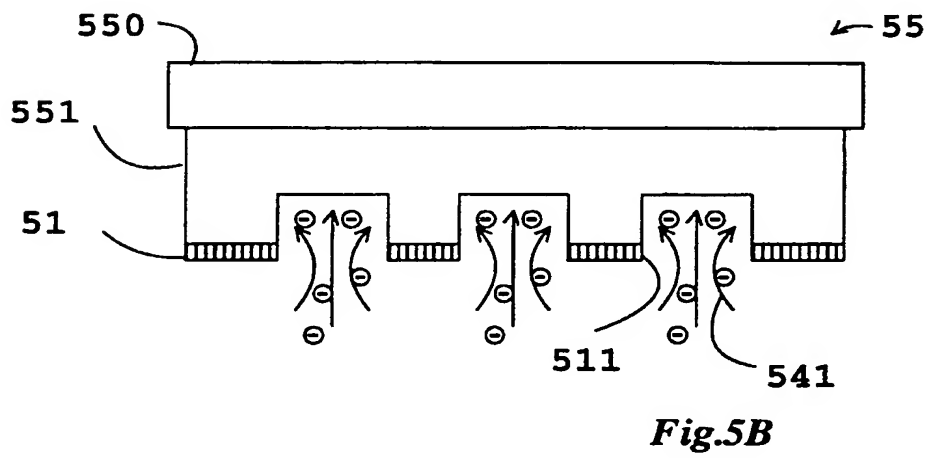
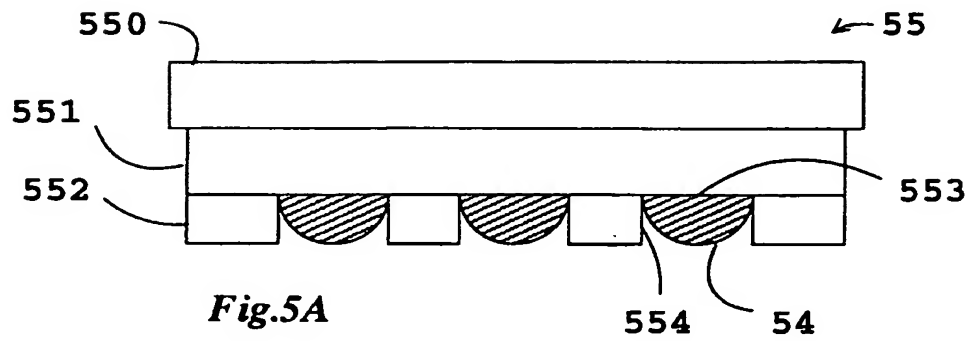
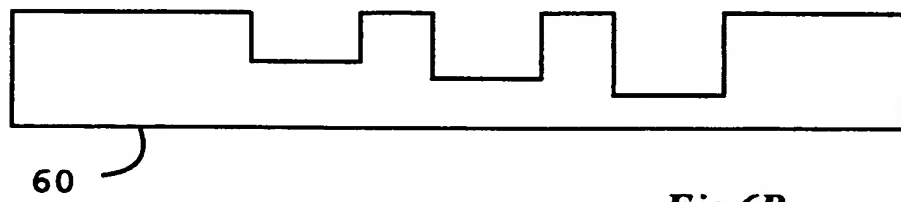
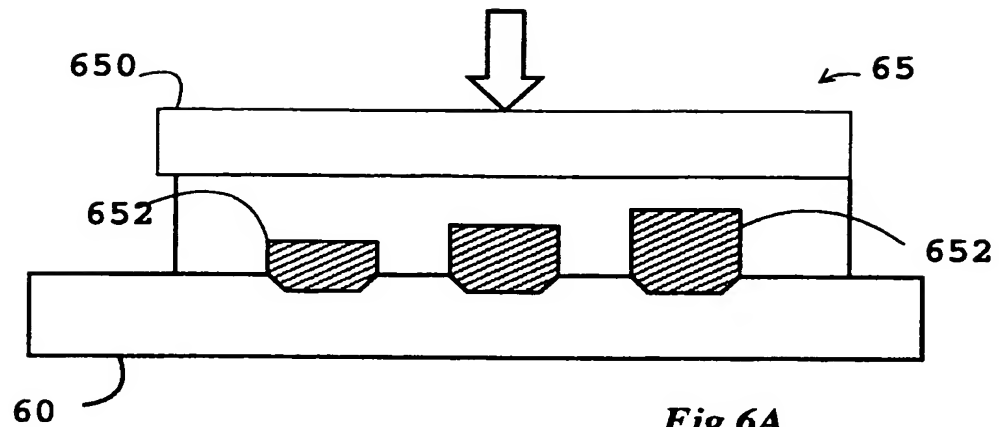


Fig. 4B

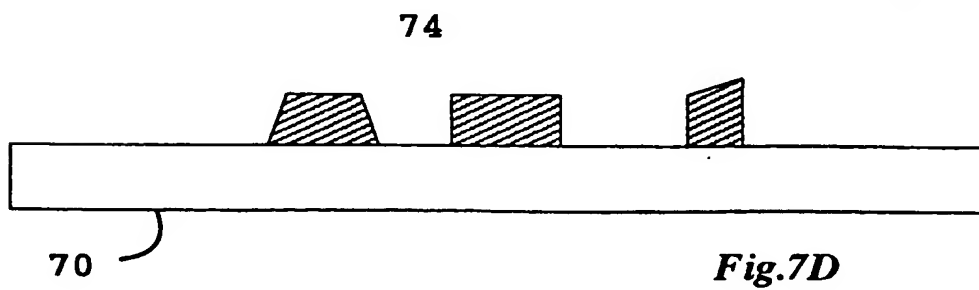
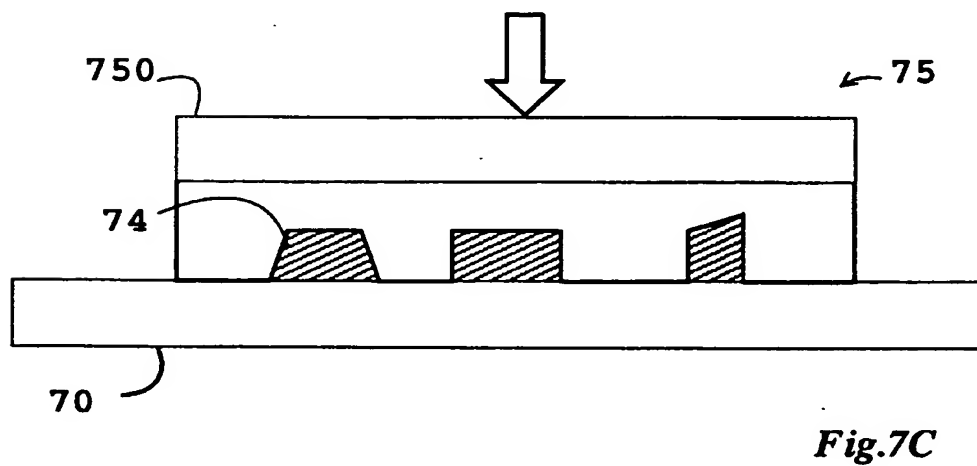
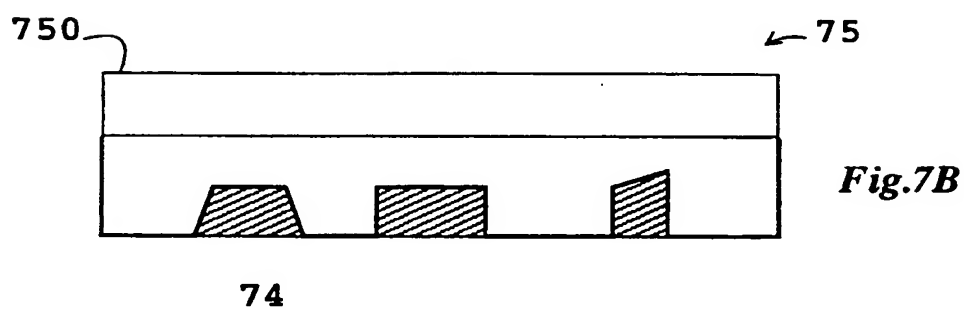
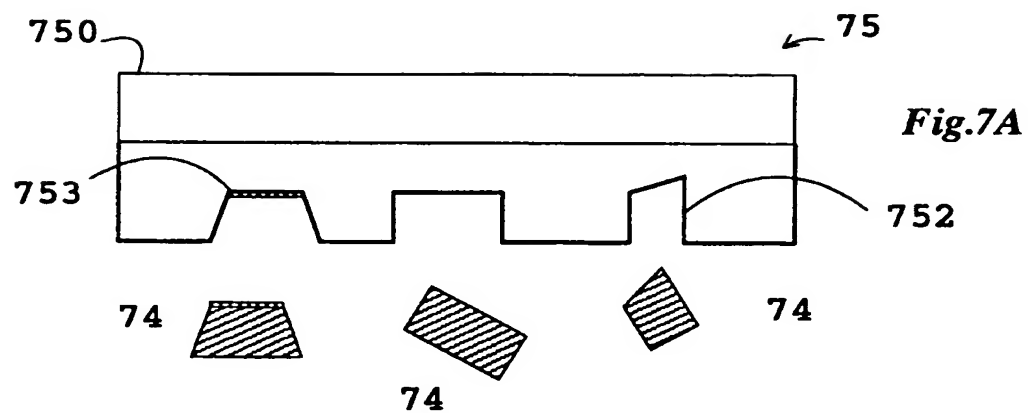
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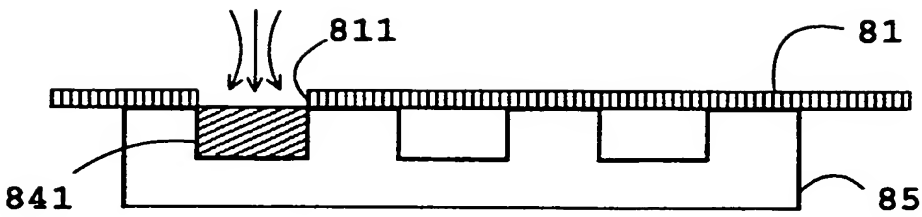


Fig.8A

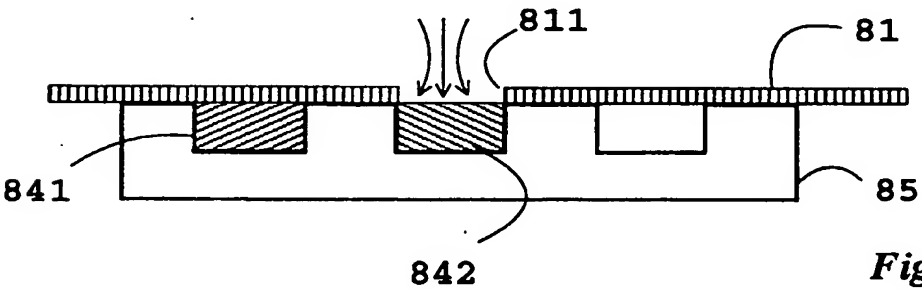


Fig.8B

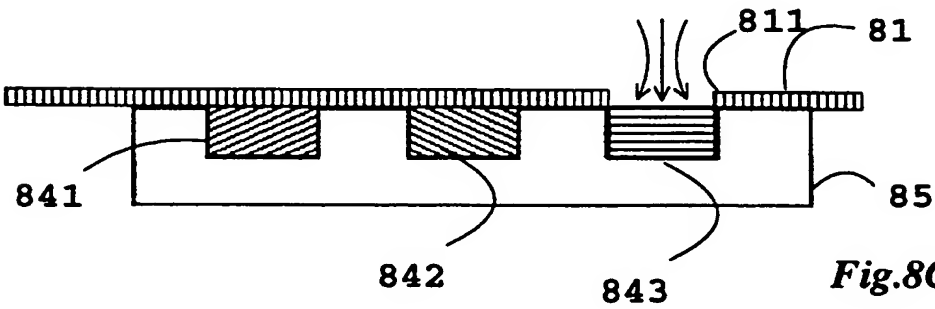


Fig.8C

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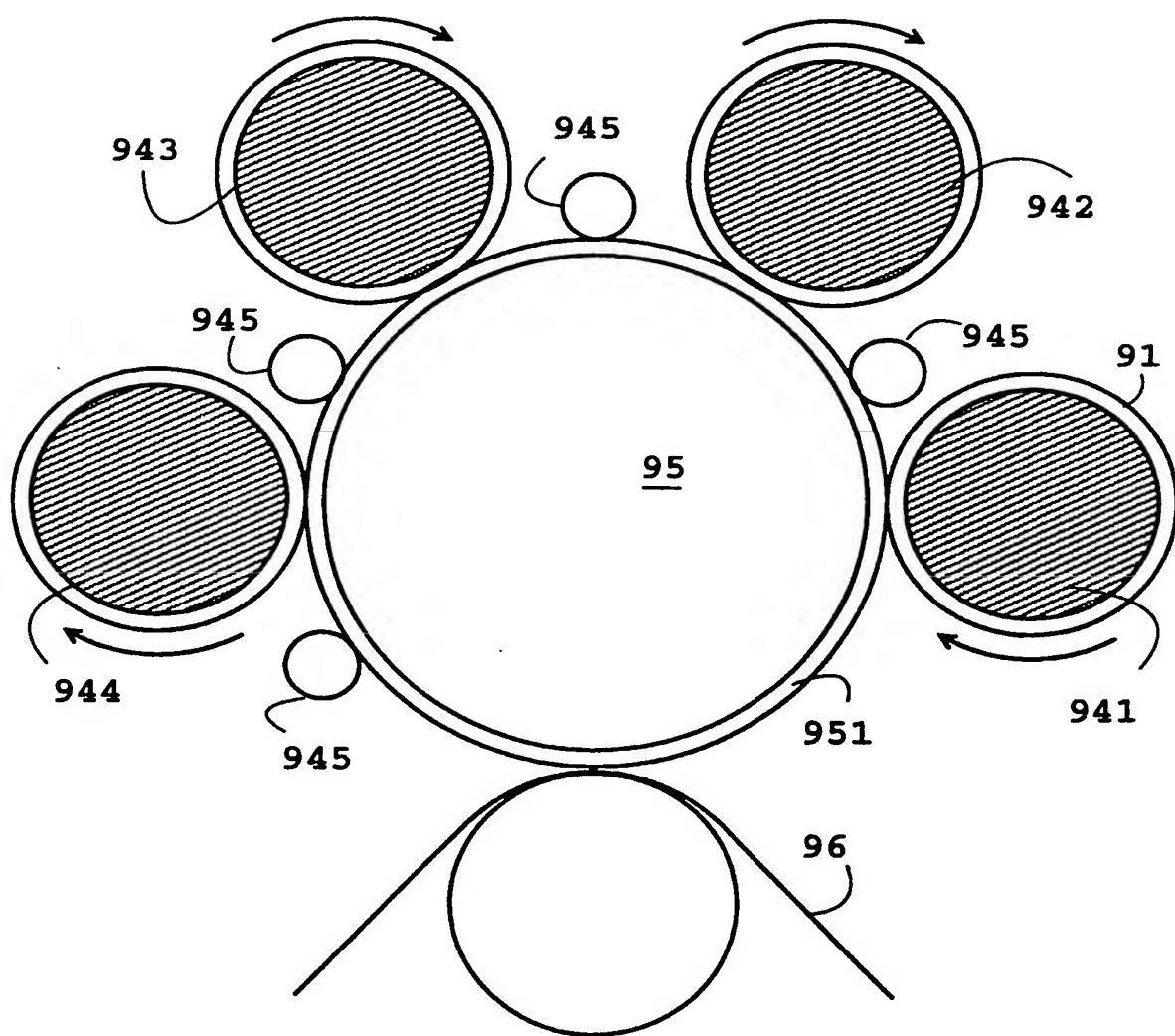


Fig.9

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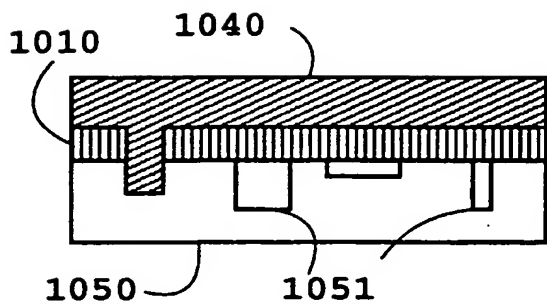


Fig.10A

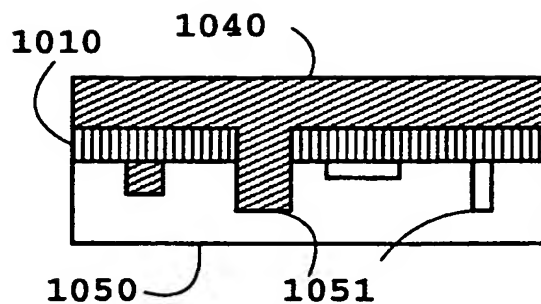


Fig.10B

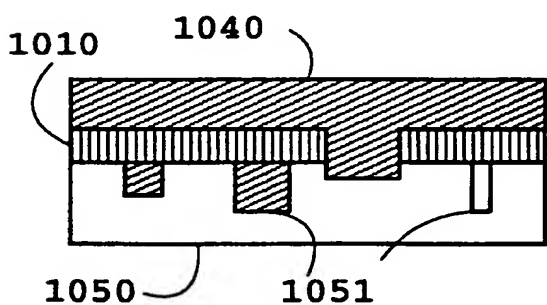


Fig.10C

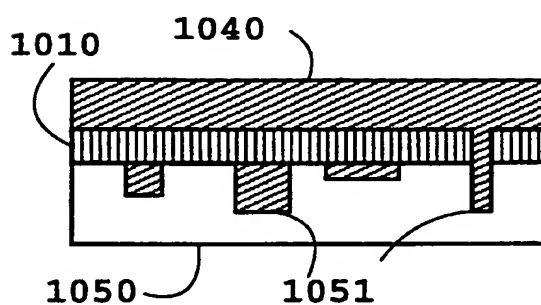


Fig.10D



Fig.10E

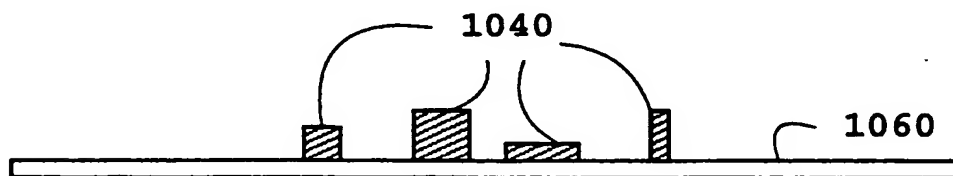


Fig.10

INTERNATIONAL SEARCH REPORT

International Application No
PC1/IB 95/00610

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 B41K1/00 G03F7/00 H01L21/768 B41C1/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 B41K G03F H01L B41C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	ADVANCED MATERIALS, vol. 7, no. 5, May 1995, WEINHEIM DE, pages 471-473, XP000533523 Y. XIA ET AL.: "Reduction of Size of Features of Patterned SAMs Generated by Microcontact Printing with Mechanical Compression of the Stamp" see the whole document ---	1-19
Y	ADVANCED MATERIALS, vol. 7, no. 7, July 1995, WEINHEIM DE, pages 649-652, XP000520481 J.WILBUR ET AL.: "Lithographic Molding : A convenient Route to Structures with Sub-Micron Dimensions" see the whole document --- -/--	1-19

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

26 April 1996

Date of mailing of the international search report

- 7. 06. 96

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Rasschaert, A

INTERNATIONAL SEARCH REPORT

Int onal Application No
PCT/IB 95/00610

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	FR,A,2 663 760 (AMRI DAHBIA) 27 December 1991 see page 2, line 3 - line 6 ---	1-19
Y	GB,A,1 431 462 (AGFA GEVAERT AG) 7 April 1976 see the whole document ---	4,5
Y	EP,A,0 583 714 (DU PONT) 23 February 1994 see the whole document ---	4,5
Y	WO,A,95 12494 (CORNING INC) 11 May 1995 see figure 2 ---	12
A	FR,A,2 516 740 (BOSCH GMBH ROBERT) 20 May 1983 see the whole document ---	12
A	US,A,5 259 926 (KUWABARA KAZUHIRO ET AL) 9 November 1993 see the whole document ---	12
A	SCIENCE, vol. 255, September 1992, US, XP002001770 M.K.CHAUDHURY ET AL.: "Correlation Between Surface Free Energy and Surface Constitution" cited in the application see the whole document -----	1

INTERNATIONAL SEARCH REPORT

Information on patent family members

In tional Application No
PCT/IB 95/00610

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
FR-A-2663760	27-12-91	NONE	
GB-A-1431462	07-04-76	DE-A- 2253944 BE-A- 806432 CA-A- 1005329 CH-A- 582723 FR-A- 2206704 JP-A- 49079240	09-05-74 24-04-74 15-02-77 15-12-76 07-06-74 31-07-74
EP-A-0583714	23-02-94	US-A- 5270078 CA-A- 2103863 JP-A- 6219069	14-12-93 15-02-94 09-08-94
WO-A-9512494	11-05-95	NONE	
FR-A-2516740	20-05-83	DE-A- 3225483 GB-A,B 2110162 JP-A- 58091695	26-05-83 15-06-83 31-05-83
US-A-5259926	09-11-93	JP-A- 5080530	02-04-93